

# Annotated Bibliography and Guide to Products of the LEDO Bioaccumulation and Adverse Effects Work Unit

by Victor A. McFarland and A. Susan Jarvis

**PURPOSE:** This technical note provides references to publications produced under the U.S. Army Engineer Long-Term Effects of Dredging Operations (LEDO) Program describing research in bioaccumulation of contaminants and the effects of chemical residues in organisms exposed to contaminated dredged sediments. The references are grouped according to subject and are accompanied by abstracts and links to on-line full text where available.

BACKGROUND: Major Federal environmental legislation passed in the 1970's included the Clean Water Act (CWA of 1972) and the Marine Protection, Research, and Sanctuaries Act (MPRSA of 1972) – both of which contained Sections requiring that the Corps undertake studies to determine the environmental effects of dredged material disposal and develop methods for minimizing adverse effects. As a result, the Dredged Material Research Program (DMRP) was initiated in 1973 and provided the first definitive information on the impacts of dredged material disposal. The DMRP was planned and budgeted as an intensive 5-year, and \$5-million effort. Although a great deal was learned during the DMRP, it was only possible to scratch the surface of the complex interrelationships determining the movements and effects of chemical contaminants in the sediment-water-biota ecosphere. Long-term effects could not be studied during the short life of the DMRP, but their existence was recognized, and legislation mandated that they be addressed. To respond to this need, the LEDO Program was initiated and the first work units (WUs) were funded in October of 1980. Two of these addressed bioaccumulation: WU No. 31772, "Toxic Substances Bioaccumulation in Aquatic Organisms," and WU No. 31773, "Environmental Interpretation of Consequences of Bioaccumulation." The first was directed at understanding the processes determining bioavailability and governing rates and magnitude of bioaccumulation, and the second addressed the effects of bioaccumulated residues. In 1995 the two work units were consolidated as WU No. 374-7, "Bioaccumulation Potential and Adverse Effects," which was concluded in September 2000. In the 20 years spanning the lifetime of this research on bioaccumulation, about 50 journal articles, technical reports, miscellaneous papers, and other forms of information exchange were published. Numerous presentations were given at symposia, conferences, and workshops, and Internet-accessible databases were created. The LEDO bioaccumulation work units provided fundamental input to the "Green Book" and the "Inland Manual" - the two implementation manuals for the ecological assessment of dredged material for placement in waters of the United States according to the requirements of the CWA and MPRSA. This technical note summarizes the LEDO bioaccumulation work units and lists the publications that resulted from them.

### **CONTENTS** (by subject):

| Analytical Methods                    | 2                  |
|---------------------------------------|--------------------|
|                                       |                    |
|                                       |                    |
|                                       |                    |
| · · · · · · · · · · · · · · · · · · · |                    |
| 1 0                                   |                    |
| · · · · · · · · · · · · · · · · · · · |                    |
|                                       |                    |
|                                       |                    |
|                                       |                    |
|                                       | Analytical Methods |

#### ANNOTATED BIBLIOGRAPHY:

#### I. Analytical Methods

Choudhury, S., Karara, A. H., Ace, L. N., and McFarland, V. A. (1990). "High performance liquid chromatographic method for the determination of 3-methylcholanthrene in channel catfish plasma," *Journal of Chromatography* 534, 208-213.

3-Methylchloanthrene (3MC) is one of the most efficient inducers of hepatic microsomal enzymes. The degree of induction depends on the concentration in the blood/liver of the animal as well as on the duration of exposure. Of the methods currently available for measuring 3MC, few are suitable for pharmacokinetic studies. This paper describes a simple, rapid, and reproducible assay for the determination of 3MC in catfish plasma. Sample preparation requires minimal time and labor, and chromatography is complete within 10 min for each run.

Honeycutt, M. E., McFarland, V. A., and McCant, D. D. (1995). "A comparison of three lipid extraction methods," (1) Bulletin of Environmental Contamination and Toxicology 55(3), 469-472. (2) Environmental Effects of Dredging Technical Note EEDP-01-35. U.S. Army Engineer Research and Development Center, Waterways Experiment Station, Vicksburg, Mississippi. http://www.wes.army.mil/el/dots/eedptn.html

Bioaccumulation studies involving neutral organic chemicals in nearly all cases require the simultaneous determination of lipid content. However, the methods for lipid measurement are not standardized and the variability among them makes comparisons across studies difficult. Sources of variability include solvents used, mixtures of solvents, and size of the sample. The purpose of this study was to assess sources of variability by comparing percent lipid determinations made on different sample sizes of the same homogenized fish tissue. Three commonly used methods were compared: (1) chloroform/methanol (Bligh-Dyer), (2) hexane/acetone, and (3) dichloromethane. Six sample sizes of frozen commercial whiting fish filets representing a 200-fold range of tissue weights ranging from 0.5 g to 50 g were extracted using each method. Results indicated that when sample sizes of 5-10 g were used, all three methods produced similar results. Variability was greatest when extracting samples less than 5 g.

McCant, D. D., Inouye, L. S., and McFarland, V. A. (1999). "A one-step ASE extraction method for TCDD TEQ determination," Bulletin of Environmental Contamination and Toxicology 63, 282-288.

The high cost of chemical analysis for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and TCDD-like compounds has led to the use of cell-based assays for determining TCDD equivalents (TCDD EQs). This investigation was aimed at producing a rapid method for sediment extract preparation for use in determining TCDD EQs in cell-based assays. Two extraction methods (the DIONEX Accelerated Solvent Extraction (ASE<sup>TM</sup>) technique and the traditional Soxhlet method) were used to extract contaminated river sediments. The extracts obtained by the two methods were compared using the Reuber H4IIE rat hepatoma cell line. The ASE method was also modified to obtain sulfuric acid/silica gel (SA/SG) clean-up of PAH compounds simultaneously with the extraction, thus eliminating the need for a separate cleanup step. Extraction efficiencies were determined for both ASE and ASE one-step methods using <sup>3</sup>H-TCDD, while efficacy of sulfuric acid silica gel (SA/SG) procedures for removal of PAHs was determined by spiking a clean sediment with a PAH standard prior to analysis with the H4IIE cell line.

Six samples of Saginaw River sediments were extracted with the ASE and Soxhlet methods and TCDD EQs were determined for each replicate sample. The averaged TCDD EQ was 237±55 pg TCDD EQ/g for the ASE and 216±107 pg TCDD EQ/g sediment for the Soxhlet method. These concentrations were not significantly different by t-test. When using the H4IIE cell line to determine TCDD EQs, it is important that the extract cleanup method remove all PAHs, as small amounts of PAHs bleeding through the column will cause induction of EROD activity and falsely elevate the measured TCDD EQ. The standard ASE method, coupled with the SA/SG column and the ASE one-step method, demonstrated equal effectiveness in removing PAHs. The one-step ASE extraction and cleanup procedure described in this paper results in TCDD extraction and PAH cleanup efficiencies comparable to Soxhlet extraction, but requires 33 percent less time and 72 percent less solvent than Soxhlet extraction. The ASE one-step method represents a significant improvement for sample preparation in cell-based assays for TCDD EQ determination.

## II. Bioaccumulation in Laboratory and Field Studies

**Tatem, H. E.** (1982). "Bioaccumulation of PCB by freshwater prawns and clams exposed to contaminated dredged material," *Environmental Effects of Dredging Information Exchange Bulletin Vol O-82-3*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 6 pp.

This information exchange bulletin describes two pilot experiments in which freshwater prawns, *Macrobrachium rosenbergii*, and clams, *Corbicula fluminea*, were exposed to a field-contaminated sediment to determine bioaccumulation of PCBs. Freshwater prawn tissue samples were taken at six different intervals (1 hr, 3, 7, 12, 19, and 25 days) during the exposure period of 25 days. The clam tissue samples were taken at eight different intervals (ranging between 17 hr and 30 days) during the exposure period of 30 days. Results of these studies demonstrated that freshwater prawns bioaccumulated PCBs and reached a plateau with little further change in the

concentration of PCBs from day 12 to day 25. The clams also accumulated PCBs, but after 30 days did not show evidence of reaching an uptake plateau.

**Tatem, H. E.** (1986). "Bioaccumulation of polychlorinated biphenyls and metals from contaminated sediment by freshwater prawns, *Macrobrachium rosenbergii* and clams, *Corbicula fluminea*," *Archives of Environmental Contamination and Toxicology* 15, 171-183.

Freshwater prawns, Macrobrachium rosenbergii, and clams, Corbicula fluminea, were exposed for 48 and 50 days to three concentrations of river sediment that contained environmental contaminants such as polychlorinated biphenyls (PCBs) and metals. Sediment was obtained twice during 1980 from the same location. Prawns were exposed to the first collected sediment (5-80), which contained higher concentrations of some metals and PCBs compared to the second sediment (11-80), used with the clams. The highest concentration of sediment 5-80 was toxic to the prawns; sediment 11-80 was not toxic to the clams. Tissue analyses of prawns for PCBs, as Aroclors® 1242 and 1254, demonstrated bioaccumulation. Maximum concentration of 1242 in prawns was achieved by day 7 while 1254 continued to accumulate during the initial 40 days of the exposure period. The PCB sediment bioaccumulation factors (BAF) for prawns ranged from 0.11 to 0.90 for 1242 and 0.20 to 2.30 for 1254, and were highest for animals exposed to 10 percent sediment. Analyses of clams for metals showed lead (Pb) in exposed animals at higher concentrations compared with controls. Bioaccumulation of Pb differed from PCB in that the Pb concentrations did not increase over time and concentrations were higher among animals exposed to 10 percent sediment compared to animals exposed to 100-percent sediment. Sediment 11-80 contained 99 mg/kg of Pb while exposed animals, at 48 days, contained approximately 2.2 mg/kg Pb. Analysis of clams for cadmium (Cd) showed exposed animals contained less Cd than controls.

McFarland, V. A., and Peddicord, R. K. (1986). "Assessment of potential bioaccumulation from Toledo and Toronto Harbor Sediments," Evaluation of Sediment Bioassessment Techniques: Report of the Dredging Subcommittee to the Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario, 51-74.

This report describes studies of the potential for bioaccumulation of contaminants from Toledo and Toronto harbor sediments by aquatic organisms conducted by the Environmental Laboratory of the USAE Waterways Experiment Station, Vicksburg, MS. Three species of freshwater fish and a bivalve organism were used as the experimental organisms. The three species of fish used were fathead minnows (*Pimephales promelas*), Japanese medaka (*Oryzias latipes*), and golden shiner minnows (*Notemigonus crysoleucas*). The bivalve molluscs tested were Asiatic clams (*Corbicula fluminea*). The exposure system was a flow-through constant-temperature exposure system consisting of twenty-four 75-L aquaria. Nominal initial concentrations of suspended particulate (SP) material were 1000 mg/L<sup>-1</sup> = high SP, 250 mg/L<sup>-1</sup> = medium SP, and 25 mg/L<sup>-1</sup> = low SP. Samples were taken for background contaminant residue determinations from culture stocks at the time exposures were begun, and at 24, 48, 96, and 240 hr of exposure for all organisms. Exposure of medaka and clams to deposited-phase sediments was continued for 30 days and samples of these organisms were also taken at that time.

Compared to many other harbor sediments, Toledo and Toronto harbor sediments were low in all contaminants included in the priority pollutant scan and contained no chemicals of any kind in unusually high concentrations. Few contaminants were above detection limits by priority pollutant scans of the sediments. The contaminants present were at low concentrations and incorporated into the sediments in such a way that their bioavailability and bioaccumulation potentials under severe exposure conditions were low. Mortality of any of the test species was not attributed to contaminants in the sediments.

The results of this study indicate a low order of chemical contamination in the sediment samples provided. Of the recognized "problem" chemicals, there was no indication of high presence or transport from sediments to organisms. These results must be considered conclusive in eliminating the sediments provided and evaluated as having high potential for bioaccumulation. Projection of these assessments to in situ sediment potential for adverse impact should be done very cautiously and always bearing in mind the representativeness of the samples in characterizing the whole area of interest.

Clarke, J. U., Lutz, C. H., and McFarland, V. A. (1988). "Influence of environmental variables on bioaccumulation of mercury," *Environmental Effects of Dredging Technical Note EEDP-01-14*. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 14 pp. http://www.wes.army.mil/el/dots/eedptn.html

The high capacity Flow-through Aquatic Toxicology Exposure System (FATES) was used in a study in which killifish (Fundulus heteroclitus) and clams (Rangia cuneata) were exposed to mercury-contaminated suspended sediment from Berry's Creek, New Jersey. Six experimental regimes were used in which temperature varied from 12 to 25 °C and salinity varied from 0.5 to 6.0 % Suspended sediment levels were maintained at 0, 5, 15, 25, 50, and 100 mg/L and all other exposure parameters were held constant during the 7-day runs. In addition to suspended sediment at the stated levels, each aquarium also contained 1-2 L bedded Berry's Creek sediment screened to allow circulating water contact, but preventing direct contact of biota. Killifish and clams were acclimated for 10 days to exposure conditions in clear water before the start of each run. Clams exposed to mercury-contaminated sediments accumulated significant amounts of mercury during all runs compared to clams that were not exposed to suspended sediment. Killifish accumulated significant Hg levels only in the aquaria with 6.0 % salinity at 25 °C. In all runs Hg levels were significantly higher in clams than in fish. Mercury uptake by killifish was clearly not influenced by temperature, salinity, or concentration of mercury-contaminated suspended sediment. Mercury uptake in the clams appeared to be slightly enhanced by increasing salinity and increasing concentrations of mercury-contaminated suspended sediment. Mercury content of the sediment from which the suspended particulate slurries were prepared ranged from 80 to 100 ppm. This was two to three orders of magnitude greater than the Hg concentrations in tissues of animals exposed to the slurries.

#### III. Databases and Software

**Dillon, T., and Gibson, A.** (1987a). "Computerized database for interpretation of the relationship between contaminant tissue residues and biological effects in aquatic organisms," *Environmental Effects of Dredging Technical Note EEDP-01-6*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 6 pp. <a href="http://www.wes.army.mil/el/dots/eedptn.html">http://www.wes.army.mil/el/dots/eedptn.html</a>

This technical note provides initial information on the format and applications of a computerized database for sublethal effects of contaminants in aquatic organisms. The objective of this work is to provide Corps elements with numerical as well as descriptive tools for relating contaminant tissue residues to biological effects in aquatic organisms in an accurate, consistent, and technically defensible fashion.

**Dillon, T. M., and Lutz, C. H.** (1991). "A computer-assisted expert system for interpreting the consequences of bioaccumulation in aquatic animals (COBIAA)," *Environmental Effects of Dredging Information Exchange Bulletin Vol D-91-4*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 5 pp.

An expert system (COBIAA) is being developed to facilitate interpreting bioaccumulation test results. Regulatory decisions concerning dredged material are based on data from toxicity tests and bioaccumulation tests. Bioaccumulation tests are conducted to demonstrate whether environmental contaminants have the potential for moving from the sediment matrix into aquatic animals. If bioaccumulation occurs, it must be possible to interpret its importance in terms of the potential for adverse effects on populations and communities of organisms. The COBIAA computer-assisted expert system is a first attempt at providing a sound technical framework for interpreting bioaccumulation data. No programming or advanced computing skills are required to use COBIAA.

Lutz, C. L., Markstrom, E., Dillon, T. M., Wright, J. R., and Houck, M. H. (1992). "A computer-assisted expert system for interpreting the consequences of bioaccumulation in aquatic animals (COBIAA)," *Environmental Effects of Dredging Technical Note EEDP-01-27*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 8 pp. http://www.wes.army.mil/el/dots/eedptn.html

This technical note describes a prototype expert system being developed to assist managers and scientists in the interpretation of bioaccumulation test results and their potential effect on the disposal of dredged material. This is a microcomputer-(MS-DOS<sup>TM</sup>) based system, operating in the Microsoft Windows<sup>TM</sup> environment. COBIAA is a decision support system designed to provide a consistent and easy-to-use method for interpreting bioaccumulation tissue residue data as applied to dredged material disposal. The objective of COBIAA is to provide a consistent nationwide methodology for interpreting bioaccumulation data.

Lutz, C. L., and McFarland, V. A. (1994). "The contaminants bulletin board system – a database of contaminated sediment information," *Environmental Effects of Dredging Information Exchange Bulletin Vol D-94-2*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 7 pp.

The Contaminants Bulletin Board is an open system that makes available databases on sediment contamination with dioxins, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons, and serves as an exchange medium for its users. Access to the bulletin board is explained as well as the procedures for finding and extracting data from the Contaminants Database. A glossary of terms is also provided.

Lutz, C. L., and McFarland, V. A. (1995). (1) "The contaminants and accumulation factor databases," Environmental Effects of Dredging Information Exchange Bulletin Vol D-95-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 7 pp. (2) "The contaminants bulletin board system – a database of contaminated sediment information," World Dredging, Mining & Construction 31(5), 15-19.

The Accumulation Factor Database provides access to experimentally obtained accumulation factors for many chemicals and organisms. This information is used to estimate the bioaccumulation potential of neutral organic chemicals in sediments. The Accumulation Factor Database was originally planned to be a separate program accessed by the Contaminants Bulletin Board System described in Lutz and McFarland (1994). System users provided feedback that resulted in combining the Accumulation Factor Database with the Contaminants Database. This action eliminated duplication between the two databases and provided a uniform platform for both types of data, allowing them to share many of the same databases and modules.

Bridges, T. S., and Lutz, C. H. (1999). "Interpreting bioaccumulation data with the environmental residue-effects database," *Environmental Effects of Dredging Technical Note EEDP-04-30*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 11 pp.

Evaluating the environmental consequences of contaminant bioaccumulation is a complex technical and regulatory problem (Bridges et al. 1996). In part, this complexity results from the fact that bioaccumulation is a measurable phenomenon, rather than an effect. Merely identifying the presence of a chemical substance in the tissues of an organism, for example, following a bioaccumulation test, is not sufficient information to conclude that the chemical will produce an adverse (toxic) effect. Because environmental contaminants vary so widely in their potential to produce toxicity, contaminant-specific information must be used to determine the potential for a bioaccumulated substance to produce adverse effects. One obvious approach to this dilemma is to interpret bioaccumulation data using published empirical data where tissue concentrations and concomitant effects have been measured in the same organism (i.e., residue-effects data). Comparison of measured tissue concentrations from bioaccumulation tests to published residue-effects information in the same or similar species offers a more direct and objective means of evaluating the potential consequences of bioaccumulation. Until recently, practical reliance on residue-effects information was hampered by the paucity of published residue-effects data and the rather "scattered" distribution of this information in the literature. Before residue-effects

information could be put to use in a regulatory program, an accessible, centralized repository for this type of data would be needed.

In recognition of this fact, the U.S. Army Corps of Engineers, with support from the U.S. Environmental Protection Agency, has developed the Environmental Residue-Effects Database (ERED). Users can query the database on-line by specifying a number of potential criteria (e.g., species, contaminant, etc.). Query results summarize relevant studies along with full citations for the original studies. Results can be printed or downloaded electronically as spreadsheet files. Currently, the ERED contains data collected from 218 studies published between 1964 and 1997. From these studies, 2,145 distinct observations have been included on-line. The ERED includes data on 229 contaminants, 119 aquatic species, and 19 effect classes (e.g., survival, growth, reproduction, enzyme inhibition, etc.). Papers involving mixtures of contaminants were excluded from the database because effects could not be linked to a specific contaminant. Although it was developed for interpretation of bioaccumulation data for the management of dredged materials, the ERED will be useful to ecotoxicologists, risk assessors, and others needing access to data that link measured tissue concentrations of contaminants to biological responses. When combined with risk-based approaches for estimating contaminant trophic transfer, the ERED is expected to provide a solid basis for making more objective determinations about the potential for "unacceptable adverse effects" resulting from contaminant bioaccumulation. The ERED has been published on the ERDC Web site and is accessible at http://www.wes.army.mil/el/ered/index.html

#### IV. Fundamentals of Bioaccumulation

McFarland, V. A., Lutz, C. H., and Reilly, F. J. (1989a). "Factors influencing bioaccumulation of sediment-associated contaminants by aquatic organisms: Factors related to contaminants," *Environmental Effects of Dredging Technical Note EEDP-01-17*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 5 pp. http://www.wes.army.mil/el/dots/eedptn.html

This is the first technical note in a series of four outlining and describing the principal factors that determine the uptake and retention of chemicals by aquatic organisms. This technical note describes factors related to contaminants. Specifically, the factors discussed in this note include: fugacity, hydrophobicity, solubility, stability, and stereochemistry.

McFarland, V. A., Lutz, C. H., and Reilly, F. J. (1989b). "Factors influencing bioaccumulation of sediment-associated contaminants by aquatic organisms: Factors related to sediment and water," *Environmental Effects of Dredging Technical Note EEDP-01-18*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 9 pp. http://www.wes.army.mil/el/dots/eedptn.html

Factors relating to sediment and water are described. Specifically, the factors discussed in this note include: (1) Sediment-related factors: Eh and pH, hydrous ferric and manganese oxides, kinetics of adsorption/desorption, oil and grease, particle interactions, sediment organic carbon, sediment particle size, sediment suspension, and (2) Water-related factors: dissolved organic carbon, hardness, and salinity.

McFarland, V. A., Lutz, C. H., and Reilly, F. J. (1989c). "Factors influencing bioaccumulation of sediment-associated contaminants by aquatic organisms: Factors related to biota" *Environmental Effects of Dredging Technical Note EEDP-01-19*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 6 pp. http://www.wes.army.mil/el/dots/eedptn.html

Factors relating to biota are described. Specifically, the factors discussed in this note include: biotransformation, depuration, diet, feeding type, kinetics of uptake and elimination, lipid content, metabolic rate, metallothioneins, and mixed-function oxidases.

McFarland, V. A., Lutz, C. H., and Reilly, F. J. (1989d). "Factors influencing bioaccumulation of sediment-associated contaminants by aquatic organisms: Glossary and bibliography," *Environmental Effects of Dredging Technical Note EEDP-01-20*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 16 pp. http://www.wes.army.mil/el/dots/eedptn.html

This is the fourth technical note in a series of four that outline and describe the principal factors determining the uptake and retention of chemicals by aquatic organisms. This technical note contains a glossary of terms and a bibliography of key and recent publications in the scientific literature containing supporting data and discussion relating to contaminants, sediment and water, and biota.

Clarke, J. U., and McFarland, V. A. (1991). "Assessing bioaccumulation in aquatic organisms exposed to contaminated sediments," *Miscellaneous Paper D-91-2*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 77 pp. + Append.

This paper synthesizes previous work on bioaccumulation to provide a working document for the environmental assessment of impacts on the aquatic environment due to bioaccumulation of sediment contaminants resulting from dredging operations and dredged material placement. Emphasis is placed on explanation of basic concepts concerning, and factors influencing, sediment contaminant bioaccumulation and bioavailability. The paper presents several numerical methods for assessing bioaccumulation, including a simple method for estimating theoretical bioaccumulation potential (TBP) from sediment chemistry for neutral organic chemicals. Methods are also given for projecting contaminant concentrations in organism tissues when steady state is achieved, based on laboratory or field exposures to contaminated sediments. These assessments are presented in the context of the U.S. Environmental Protection Agency's tiered testing approach for dredged material evaluation. The various numerical methods for bioaccumulation assessment are illustrated and compared using step-by-step example calculations with hypothetical and actual data.

## V. Interpreting Bioaccumulation

Bridges, T. S., Moore, D. W., Landrum, P., Neff, J., and Cura, J. (1996). "Summary of a workshop on interpreting bioaccumulation data collected during regulatory evaluation of dredged material," *Miscellaneous Paper D-96-1*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 26 pp. + Append.

Evaluating the environmental consequences of contaminant bioaccumulation resulting from dredged material disposal is a complex technical and regulatory problem. This problem is exacerbated by the high cost of bioaccumulation testing and the lack of explicit guidance on how bioaccumulation data should be interpreted and used within a regulatory program. The way bioaccumulation data are interpreted during evaluations of dredged material must be technically defensible and cost-efficient. In response to problems related to the interpretation of bioaccumulation data, the U.S. Army Corps of Engineers (USACE) and the U.S. Environmental Protection Agency (USEPA) held a joint bioaccumulation workshop in Denver, CO, on 29-31 August 1995. The purpose of the workshop was to determine if more effective regulatory guidance could be developed for interpreting the effects of bioaccumulation from data currently collected during the evaluations of dredged material. Workshop participants were from USACE, USEPA, U.S. Fish and Wildlife Service, National Oceanic and Atmospheric Administration, Department of Defense, academia, and the private sector. Short- and long-term recommendations are made for interpreting bioaccumulation data to ensure the protection of human health and aquatic and terrestrial wildlife.

Bridges, T. S., Moore, D. W., McFarland, V. A., Wright, T. D., Wilson, J. R., and Engler, R. M. (1996). "Proposed new guidance for interpreting the consequences of bioaccumulation from dredged material," *Environmental Effects of Dredging Technical Note EEDP-01-41*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 10 pp. http://www.wes.army.mil/el/dots/eedptn.html

Modifications to current guidance for evaluating and interpreting bioaccumulation data collected during regulatory evaluations of dredged material are suggested. Guidance given was based on the four-tiered framework for the evaluation of dredged material. The guidance suggested in this technical note differs from existing guidance in two important respects: (1) development of site-specific lists for the bioaccumulating chemicals of concern (BCCs), assessment endpoints, and measurement endpoints will ensure that site-specific questions are well thought out and explicitly defined, and, (2) comparison of tissue contaminant concentrations with relevant residue-effects data emphasizes the need to evaluate effects data in order to determine the potential for "unacceptable adverse effects."

#### VI. Pharmacokinetics of Bioaccumulation

Karara, A. H., and McFarland, V. A. (1992). "A pharmacokinetic analysis of the uptake of polychlorinated biphenyls (PCB) by Golden Shiners," *Environmental Toxicology and Chemistry* 11, 315-320.

A 96-hr, static, nonconstant exposure design was used to assess pharmacokinetic parameters and to identify the rate-limiting process in polychlorinated biphenyl (PCB) uptake by golden shiners (Notemigonus crysoleucas). Fish were exposed individually to <sup>14</sup>C-labeled PCBs corresponding to Aroclor 1254 (A1254). After various intervals (2-96 hr), fish and water were analyzed for total radioactivity. Uptake of PCBs and decline of the external water concentration were both rapid. A clearance constant-based, one-compartment model was used to represent the fish. Model-based equations for PCB concentrations in the fish and in the water were fitted simultaneously to the observed data with the PCNONLIN63 computer program. The absorption

clearance constant was 30.8 ml  $h^{-1}$   $g^{-1}$  fish, which identified gill blood flow as the uptake rate-controlling process. The model-predicted apparent volume of distribution  $V_d$  and bioconcentration factor  $K_b$  were 5,280 ml/g fish and 9,059 ml water per gram fish, respectively. The model-predicted elimination rate constant  $k_e$  was 5.84 x  $10^{-3}$   $h^{-1}$ , corresponding to a  $t_{1/2}$  of 4.9 d.

McFarland, V. A., Feldhaus, J., Ace, L. N., and Brannon, J. M. (1994). "Measuring the sediment/organism accumulation factor of PCB-52 using a kinetic model," *Bulletin of Environmental Contamination and Toxicology* 52(5), 699-705.

In theory, the accumulation factor AF, describing the equilibrium distribution of any neutral organic chemical between the organic phases represented by sediment organic carbon and organism lipid can be approximated by the single value 1.7. Theoretical expectations of constancy notwithstanding, empirical observations have produced a range of values. Most of the studies that have measured AFs, whether in the laboratory or in the field, have involved infaunal, sediment-processing polychaetes, clams, and amphipods. Laboratory exposures have been continued for up to 6 months in order to achieve steady-state tissue levels of bioaccumulating chemicals so that AFs could be calculated. Kinetic modeling using short exposures provides an alternative to the long-term exposures required to reach plateaus, and in so doing, can potentially eliminate many of the factors producing variability in the result. In this study, a threecompartment closed kinetic model was used in 5-day exposures of fathead minnows, with frequent, exponentially spaced, sequential sampling to model the distribution of PCB-52 among fish, suspended sediment, and water. Steady-state projections using the model were the basis for calculation of an AF = 2.34 for PCB-52. This result is much less than a factor of two greater than the theoretical value. Advantages and disadvantages of using the kinetic approach are discussed.

#### VII. Polychlorinated Biphenyls and Dioxins

McFarland, V. A., Clarke, J. U., and Gibson, A. B. (1986). "Changing concepts and improved methods for evaluating the importance of PCBs as dredged sediment contaminants," *Miscellaneous Paper D-86-5*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 18 pp. + Append. NTIS No. AD A174 177

This paper summarizes the current understanding of the chemical nature of polychlorinated biphenyls (PCBs), the factors determining their persistence and potential to bioaccumulate, and the characteristics of individual PCB congeners that determine their widely differing potencies and modes of toxic effect.

PCBs are highly persistent and widespread contaminants frequently encountered by Corps of Engineers personnel involved with dredged material disposal activities. Interpretation of the potential ecological effects of disposing of PCB-contaminated sediments in open water or using other methods is a persistent difficulty in the preparation of environmental impact statements and other documentation necessary for informed decision making. However, the understanding of the nature and behavior of PCBs as environmental contaminants has progressed rapidly within the scientific community with the advances in analytical technology of the past few years.

ERDC/TN EEDP-01-47 May 2001

PCBs are a group of 209 congeners that have up to 10 chlorine atoms on the biphenyl molecule and that differ from each other in the number and positions of the chlorines. About 100 of these congeners are found in the industrial PCB formulations marketed as Aroclors, released into the environment through disposal of transformer oils and other PCB-containing products, and are now widespread in sediments. Only some of these congeners are toxic, either directly through receptor binding or indirectly through microsomal enzyme induction. Most of the congeners that are toxic, or that are otherwise important due to their prevalence or persistence in the environment, belong to the isomer groups tetra-, penta-, and hexachlorobiphenyl (i.e. they have four to six chlorine atoms per molecule).

Current evaluations of PCBs in environmental samples by quantitation as Aroclors or as total PCBs are of limited value due to degradation and differential affinities of congeners for various environmental compartments. PCBs that entered the environment as identifiable Aroclor mixtures are altered by these physical, chemical, and biological processes and cannot properly be identified by comparison with Aroclor analytical standards. Comparisons of PCB-contaminated Hudson River sediments, along with water and organism tissue samples exposed to those sediments, with Aroclor standards demonstrate the frequent lack of correspondence in PCB components between Aroclors and environmental samples.

PCBs in environmental samples can be evaluated more meaningfully by quantitation as totals in the isomer groups di- through decachlorobiphenyl (two to ten chlorines per molecule). This has the advantage of indicating the relative concentrations of the groups potentially containing the most toxic and bioaccumulating congeners. Furthermore, recent advances in analytical techniques are making the analysis of individual congeners more feasible. Thus, attention can be focused specifically on the PCB components that are important on the basis of toxicity, persistence, and prevalence, allowing a more accurate assessment of the environmental effects of various dredged material disposal options than is currently available.

Clarke, J. U., McFarland, V. A., and Pierce, B. D. (1989). "Preliminary recommendations for a congener-specific PCB analysis in regulatory evaluation of dredged material," *Miscellaneous Paper D-89-2*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 32 pp. + Append.

A preliminary recommendation of priority polychlorinated biphenyl (PCB) congeners for congener-specific analysis is offered for use in the regulatory evaluation of dredged material. Potential toxicity, environmental prevalence, and relative abundance in animal tissues are the criteria used in the selection of specific congeners and their assignment to four priority groups. Potential toxicity is equated to mammalian microsomal mixed-function oxidase (MFO) induction activity and type. MC- (3-methylcholanthrene-) type and mixed-type induction activities are considered potentially most toxic, followed by PB- (phenobarbital-) type induction activity. Weak inducers and noninducing congeners have the least potential for toxicity. Environmental prevalence, i.e., frequency of occurrence of specific congeners in environmental samples, is determined from the literature. Relative abundances of congeners (percents of total PCB as the sum of all congener concentrations) in tissues are reported or calculated from data in the literature, along with data generated from an experiment conducted at the U.S. Army Engineer Waterways Experiment Station.

Eight congeners, IUPAC (International Union of Pure and Applied Chemists) Nos. 77, 118, 126, 128, 138, 156, 169, and 170, are assigned to Group 1. These congeners include the three potentially highly toxic MC-type MFO inducers, along with five mixed-type inducers that have frequently been reported in environmental samples. Group 2 congeners are PB-type MFO inducers that are also prevalent in the environment; these include Nos. 87, 99, 101, 153, 180, 183, and 194. These two groups are considered most likely to contribute to any adverse biological effects associated with PCBs in an environmental sample. Group 3 congeners, Nos. 18, 44, 49, 52, 70, 74, 151, 177, 187, and 201, are weak or noninducers, but they occur frequently in the environment or in high concentrations in animal tissues relative to other PCB congeners, and thus may be of concern. Of possible importance are congeners 37, 81, 105, 114, 119, 123, 157, 158, 167, 168, and 189. These Group 4 congeners are mixed-type inducers that have been reported infrequently and in relatively low tissue concentrations.

McFarland, V. A., and Clarke, J. U. (1989). "Environmental occurrence, abundance, and potential toxicity of polychlorinated biphenyl congeners: Considerations for a congener-specific analysis," *Environmental Health Perspectives* 81, 225-239.

Polychlorinated biphenyls (PCBs) as environmental contaminants often cannot be adequately described by reference to Aroclors or to total PCBs. Although there are 209 PCB configurations (congeners), perhaps half that number account for nearly all of the environmental contamination attributable to PCBs. Still fewer congeners are both prevalent and either demonstrably or potentially toxic. If potential toxicity, environmental prevalence, and relative abundance in animal tissues are used as criteria, the number of environmentally threatening PCB congeners reduces to about 36. Twenty-five of these account for 50 to 75 percent of total PCBs in tissue samples of fish, invertebrates, birds, and mammals.

A few PCB congeners that are sterically similar to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) are directly toxic. Other PCB congeners, as well as those that are directly toxic, may also be involved in toxicity indirectly by stimulating the production of (inducing) bioactivating enzyme systems. The most consequential of these have the ability to induce aryl hydrocarbon metabolizing mixed-function oxidases (MFOs). An increased capacity for bioactivation of otherwise nontoxic foreign compounds such as certain polynuclear aromatic hydrocarbons (PAH) to cytotoxic or genotoxic metabolites can result. The effectiveness of specific PCB congeners as inducers of different types of cytochrome P-450-dependent MFO systems is determined by their stereochemistry. Although MFO induction is not a proximate cause, it is a strong correlate of certain kinds of toxicities. Structural patterns can thus be used to discriminate among PCB congeners on the basis of toxic potential, if not entirely on toxicity per se. Congeners that demonstrate 3-methylcholanthrene-type (3-MC-type) and mixed-type MFO induction have the greatest toxic potential. These congeners most closely resemble 2,3,7,8-TCDD in their structures, and in their toxic effects the larger group of phenobarbital-type (PBtype) inducers have considerably less potential for contributing to toxic effects. Weak inducers and noninducing congeners have the least potential for toxicity.

Using the rationale described in this paper, the most environmentally threatening PCB congeners were assigned to four groups. Congeners assigned to Group 1 are considered most likely to contribute to adverse biological effects attributable to PCBs in an environmental sample.

Group 1A contains the three most potent (pure 3-MC-type inducer) congeners, IUPAC Nos. 77, 126, and 169. Six congeners, Nos. 105, 118, 128, 138, 156, and 170, are assigned to Group 1B. These congeners are mixed-type inducers that have been reported frequently in environmental samples. Group 2 congeners are PB-type inducers that are also prevalent in the environment; these include Nos. 87, 99, 101, 153, 180, 183, and 194. Group 3 congeners, Nos. 18, 44, 49, 52, 70, 74, 151, 177, 187, and 201, are weak or noninducers, but they occur frequently in the environment or in high concentrations in animal tissues relative to other PCB congeners, and so may be of concern. Of possible importance are congeners 37, 81, 114, 119, 123, 157, 158, 167, 168, and 189. These are mixed-type inducers that have been reported infrequently in biota and in very low tissue concentrations and are assigned to Group 4.

McFarland, V. A., Clarke, J. U., and Ferguson, P. W. (1993). "Dioxin in sediments: Application of toxic equivalents based on international toxicity equivalency factors to regulation of dredged material," *Environmental Effects of Dredging Technical Note EEDP-04-18*, Environmental Laboratory, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 12 pp. http://www.wes.army.mil/el/dots/eedptn.html

This technical note explains the origin and meaning of the dioxin toxic equivalent (TEQ) concept, reviews the application of TEQs to dredged sediment evaluations, and describes the use of TEQs in regulatory decision-making processes involving dioxin-containing dredged sediments. Shortcomings in the present use of TEQ methodology are described and supported by examination of recent cases where TEQs have been used in regulatory decisions. An alternative approach based on bioassay-derived TEQs shows promise in overcoming many of the problems associated with TEQs as currently derived from chemical analysis.

VIII. Residue Effects

**Dillon, T. M.** (1984). "Biological consequences of bioaccumulation in aquatic animals: An assessment of the current literature," *Technical Report D-84-2*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 35 pp. + Append. NTIS No. AD A144 161.

This report presents, in narrative and tabular form, an analysis and the results of a literature search conducted to determine the sublethal effects of environmental pollutants on aquatic organisms. It also identifies those biological response parameters that are to be used for scientific interpretive guidance on the consequences of bioaccumulation.

**Dillon, T. M., and Gibson, A. B. (1985).** "Bioaccumulation and effects on reproduction in aquatic organisms: An assessment of the current literature," *Miscellaneous Paper D-85-2*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 18 pp. + Append. NTIS No. AD A163 202.

An analysis of results of a literature search conducted to examine the effects on reproduction in aquatic animals is presented in narrative and tabular form. A method is described whereby tissue concentrations can be estimated (using published bioconcentration factors) from data reported in the literature where reproductive effects, but not tissue data, were reported. An initial

compilation of information is provided for decision makers who seek general guidance in interpreting bioaccumulation results, as well as for decision makers with site-specific concerns.

**Dillon, T. M, and Gibson, A. B.** (1987b). "Use of Daphnia magna to predict consequences of bioaccumulation," *Environmental Effects of Dredging Technical Note EEDP-01-07*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 13 pp. <a href="http://www.wes.army.mil/el/dots/eedptn.html">http://www.wes.army.mil/el/dots/eedptn.html</a>

This technical note represents a portion of the laboratory research evaluating the relationship between mercury and cadmium tissue residues and biological effects in the freshwater crustacean, *Daphnia magna* (commonly known as the water flea). Procedures are presented in this note for a 28-day *Daphnia magna* toxicity test. Results indicated that *Daphnia* with tissue concentrations greater than or equal to 5.5 µg/g mercury or 11.8 µg/g cadmium demonstrated diminished survival, growth, and reproduction. The 28-day *Daphnia magna* toxicity test may be used to predict safe and harmful levels of mercury and cadmium for *Daphnia magna* when screening for water-column toxicity resulting from open-water disposal of a specific dredged material.

**Dillon, T. M.** (1988). "Relationship between PCB tissue residues and reproductive success of fathead minnows," *Environmental Effects of Dredging Technical Note EEDP-01-13*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 9 pp. <a href="http://www.wes.army.mil/el/dots/eedptn.html">http://www.wes.army.mil/el/dots/eedptn.html</a>

This technical note provides initial guidance for interpreting the biological consequences of bioaccumulation in aquatic organisms. Specifically, the relationship between polychlorinated biphenyl (PCB) tissue residues and reproductive success in the fathead minnow, *Pimephales promelas*, is examined. Results from the testing of adult fathead minnows indicated that PCB-contaminated sediments had a significant deleterious effect on species fecundity and frequency of reproduction.

Gibson, A. B., and Dillon, T. M. (1989). "Bioaccumulation of chlorinated contaminants and concomitant sublethal effects in marine animals: An assessment of the current literature," Environmental Effects of Dredging Technical Note EEDP-01-15, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 14 pp. http://www.wes.army.mil/el/dots/eedptn.html

This technical note focuses on studies evaluating the sublethal effects of chlorinated organic contaminants on marine and estuarine organisms. The two objectives of this note are: (1) to survey the literature for papers reporting both the sublethal effects of organohalogens and the corresponding body burdens in marine fish and invertebrates, and (2) to provide a source of information for Corps field elements who have site-specific concerns. The following information was recorded for each paper included in this review: contaminant, test animal, exposure time, contaminant exposure concentration, reported tissue concentration, and any observable biological effects. The test animal was identified by common name and/or phylogenetic group. Tissue concentrations were expressed on a wet-weight basis. Exposure concentrations were reported as micrograms per liter (parts per billion) unless noted otherwise.

Dillon, T. M., Benson, W. H., Stackhouse, R. A., and Crider, A. M. (1990). "Effects of selected PCB congeners on survival, growth, and reproduction in *Daphnia magna*," *Environmental Toxicology and Chemistry* 9, 1317-1326.

The effects of individual polychlorinated biphenyl (PCB) congeners on survival, growth and reproduction in the freshwater cladoceran, *Daphnia magna*, were determined. Congeners evaluated in this study (IUPAC Nos. 52, 77, 101, 118, 138, 153, 180) represent a variety of microsomal mixed-function oxidase (MFO) inducers. After 21 days of static renewal exposure, *Daphnia* survival was high (88-100 percent) in all congener treatments and unaffected by any PCB. Polychlorinated biphenyl congeners had little to no detectable sublethal effects on reproduction and growth. The number of neonates produced was either unaffected (congeners 52, 77, 118) or enhanced (congeners 101, 138, 153, 180). Effects on the total biomass were mixed and the magnitude of significant differences, when observed, was small. Diminished biomass was observed in *Daphnia* exposed to congener 101, whereas increases occurred in treatments with congeners 52 and 118. Both elevated and diminished biomass were observed in animals exposed to congener 77. Congeners 138, 153, and 180 had no significant effect on *Daphnia* biomass.

Daphnia accumulated substantial amounts of all PCBs even though minimal effects on survival, growth, and reproduction were observed. Mean tissue concentrations ranged from approximately 2.0 ng/mg to 130 ng/mg dry weight. These tissue residues are one to several orders of magnitude greater than those observed in aquatic fish and invertebrates collected in and around industrial waterways of the Great Lakes. Possible explanations for the lack of PCB congener toxicity are discussed.

Dillon, T. M., and Gibson, A. B. (1990). "Literature review for residue-effects relationships with hydrocarbon contaminants in marine organisms," *Environmental Effects of Dredging Technical Note EEDP-01-24*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 13 pp. http://www.wes.army.mil/el/dots/eedptn.html

This literature review was executed to identify potential residue-effects relationships involving hydrocarbon contaminants, which are described in the scientific literature. Only a small proportion (approximately 10 percent) of the publications reviewed contained information on both the biological effects of hydrocarbons and the corresponding tissue residues in marine bivalves. The lack of data restricts the utility of the database to generate quantitative guidance on the hydrocarbon residue-effects relationship. Variations in analytical methods also reduce the effectiveness of any potential guidance. Some general qualitative trends were apparent from the data reviewed. The database was considered too small and does not provide any specifics regarding the 15 individual polycyclic aromatic hydrocarbons (PAHs) on the priority pollutant list.

Moore, D. W., Dillon, T. M., and Suedel, B. C. (1991). "Chronic toxicity of tributyltin to the marine polychaete worm, *Neanthes arenaceodentata*," *Aquatic Toxicology* 21, 181-198.

Life cycle toxicity tests provide ecologically relevant indices for estimating long-term 'safe' concentrations of environmental contaminants. Tissue concentrations observed in animals from

these tests can also be used to estimate the risk associated with contaminant residues in field-collected animals. Such residue-effects information was generated for the marine polychaete worm, *Neanthes arenaceodentata*, exposed to the organometal tributyltin (TBT).

Juvenile Neanthes were exposed in the laboratory to five concentrations (500, 100, 50, 10, 0 ng/l) of TBT. After ten weeks, effects on survival, growth, and reproduction were evaluated. Significant mortality (79 percent) was observed only in the highest TBT exposure concentration. Growth (dry weights of individual worms) was significantly reduced in the two highest TBT treatments. Reproduction (mean number of eggs and emergent juvenile (EJ) worms) was significantly reduced in the 100 ng/l treatment. Reproduction was not evaluated in worms from the 500 ng/l treatment due to low survival and an inability to distinguish sexes. No adverse effect on survival, growth, or reproduction was observed in worms exposed to 50 or 10 ng/l TBT. TBT had no observed effect on egg size, estimated individual EJ dry weight, or timing of reproductive events.

Neanthes arenaceodentata accumulated significant amounts of TBT, which mirrored the exposure gradient: 16.81, 6.27, 2.99, 1.47, and 0.21  $\mu$ g/g dry weight. Chronic effects were observed in worms with tissue concentrations >6.3  $\mu$ g TBT/dry weight. No significant effects were observed at tissue concentrations <3.0  $\mu$ g/g. Detectable amounts of TBT metabolites (diand monobutyltin) were found in all tissue samples, with a greater proportion found in worms with lower TBT residues. These TBT residue data are discussed in relation to comparative laboratory and field information.

**Dillon, T. M., and Gibson, A. B.** (1992). "Critical body residues (CBR) approach for interpreting the consequences of bioaccumulation of neutral organic contaminants," *Environmental Effects of Dredging Technical Note EEDP-04-17*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 12 pp. <a href="http://www.wes.army.mil/el/dots/eedptn.html">http://www.wes.army.mil/el/dots/eedptn.html</a>

This technical note describes a procedure for interpreting tissue residues of neutral organic chemicals generated in 28-day dredged material bioaccumulation bioassays. This interpretive guidance uses a critical body residue (CBR) of neutral organic chemicals reported for the fathead minnow, Pimephales promelas. The CBR is based on a very large U.S. Environmental Protection Agency (EPA) acute toxicity database and well-accepted quantitative structure activity relationships (QSARs). Guidance in this technical note is not appropriate when xenobiotic metabolism of neutral organic contaminants is likely. The procedure in this technical note is simply an additional tool for evaluating the consequences of bioaccumulation in aquatic organisms.

Emery, V. L., Jr., and Dillon, T. M. (1996). "Chronic toxicity of phenanthrene to the marine polychaete worm, Nereis (Neanthes) arenaceodentata," Bulletin of Environmental Contamination and Toxicology 56, 265-270.

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the environment. PAHs accumulate in bottom sediments and may represent a hazard to the benthos. The objective of this

ERDC/TN EEDP-01-47 May 2001

study is to evaluate the chronic sublethal effects of one PAH, phenanthrene (PHN), on the polychaete worm, *Nereis (Neanthes) arenaceodentata*.

Range-finding chronic toxicity tests were conducted using immature adult worms and 48-hr-old emergent juveniles (EJs) with and without culture sediment. Immature adult worms were exposed to five PHN concentrations and two controls and survival was determined after 14 days. The EJs were exposed to five PHN concentrations and two controls and survival was determined after 4 days. Range-finding tests indicated 20  $\mu$ g PHN/L was an appropriate sublethal concentration. EJs were set up in an 8-week chronic exposure with three treatments: 20  $\mu$ g PHN/L, seawater control, and the carrier control. Growth, effects on reproduction, and PHN tissue residues were measured after the 8-week chronic exposure.

The range-finding toxicity tests indicated that sediment had no effect on toxicity and that EJs were an order of magnitude more sensitive to PHN than adults. EJ 96-hr LC50s were identical for treatments with and without sediment,  $51 \mu g/L$ . Immature adult 14-d LC50s were also identical for treatments with and without sediment,  $501 \mu g/L$ . Survival was high among the experimental treatments following the 8-week chronic PHN exposure and was not significantly different among treatments. The acetone carrier had a significant and positive effect on growth and reproduction in comparison to the seawater control. The PHN body burden observed in this study for the polychaetes was two orders of magnitude (4.38 x  $10^{-3}$ mmol/kg) lower than expected if the effects were solely mediated via chronic narcosis. Increase in lysosomal size and membrane fragility in marine organisms has been reported in other studies with similar body burdens.

Lotufo, G. R., Farrar, J. D., and Bridges, T. S. (2000). "Effects of exposure source, worm density, and sex on DDT bioaccumulation and toxicity in the marine polychaete *Neanthes arenaceodentata*," *Environmental Toxicology and Chemistry* 19(2), 472-484.

The influence of exposure source, worm density, and sex on the bioaccumulation and toxicity of C-14-labeled DDT was evaluated for Neanthes arenaceodentata. Emergent juvenile worms were exposed to DDT-spiked sediment (SED), DDT-spiked supplemental food (TetraMarin; TM), or a combination of both (SEDTM) in 28-day toxicity experiments. concentrations in the sediment and in the food were equal on an organic carbon basis. Higher body residues were attained under the TM exposure compared to SED, indicating the importance of nonsedimentary organic matter as a source for contaminant uptake. The DDT was more bioavailable when associated with TetraMarin compared to sediment, indicating that factors other than sorption to organic carbon can influence contaminant bioavailability. Body residues as high as 0.5 mol/g wet weight were not associated with decreased survival, suggesting general narcosis as the mode of lethal toxicity of DDT to N. arenaceodentata. Most of the body burden was DDT unmetabolized compound (similar to 70 percent). Reduced growth, observed under all exposures, was significant at lower concentrations when worms were fed DDT-spiked food (TM and SEDTM). N. arenaceodentata may have detected the presence of DDT in the TetraMarin and decreased their feeding rate, at the cost of reduced growth. The influence of worm density on DDT toxicity and bioaccumulation was examined by exposing one or five worms per beaker (74 and 370 worms/m(2), respectively) to spiked sediment. Although higher body residues were attained under low density, worms exposed in groups of five were significantly more sensitive to

the effects of DDT on growth. Sex also had a large influence on DDT uptake kinetics. In sediment exposures (SED) to a trace concentration, the uptake clearance rate (mg(OC)/g lipids/h) was two times more efficient and the elimination rate was five times faster in mature males than in mature females.

IX. Thermodynamically Defined (Theoretical) Bioaccumulation Potential (TBP)

McFarland, V. A. (1984). "Activity-based evaluation of potential bioaccumulation from sediments," Montgomery, R. L.; Leach, J. W.; eds. *Dredging and Dredged Material Disposal: Proceedings of the Conference, Dredging '84*; November 14-16; Clearwater Beach, FL., New York, NY: American Society of Civil Engineers; Vol 1, 149-158.

Sediment bioaccumulation potential evaluations can be improved by a two-level approach. Chemical analysis of sediment interpreted using phase-activity considerations in first-level evaluations would serve as a screen to separate sediments having low potential for bioaccumulation of neutral chemicals from those having high potential. Level-II evaluation, if considered necessary, could then be accomplished using established biological methods to refine the evaluation made in Level I.

Bioaccumulation of chemicals from sediments as the source of contamination can be viewed as a phase-equilibrium distribution in which the phases of interest are only sediment and organism tissue. This is a simplification that has as its object determination of the maximum concentration of a chemical that could be accumulated in organism tissue given sufficient time for equilibration. Kinetic, steric, or other constraints to release of chemicals from sediment and to absorption, assimilation, and elimination are not considered. Therefore the "potential" thermodynamically defined is not necessarily the steady-state tissue concentration that could result from actual exposure.

To estimate the thermodynamically defined maximum bioaccumulation potential (TBP) of neutral chemicals in sediment, the relevant phase-pair are sediment and organism tissue. Organic carbon in sediment and lipid in an organism often represent sufficiently large components to account for most of the sorption capacity and to characterize the activity of the phase. When this is the case, it would seem appropriate to normalize concentration to unit measure of the relevant component. The activity  $\gamma_i$  of neutral chemicals in either of these organic components is very low compared with their  $\gamma_i$  in water and the ratio of the two activity coefficients can be expected to be on the order of unity. The actual difference would be difficult to measure, but can be estimated using reported free-energy relationships. In this paper it is demonstrated that bioaccumulation potential as the expected concentration in lipid of an organism can be estimated based on knowledge of the neutral chemical concentration in a sediment  $C_s$  and the sediment organic carbon fraction  $f_{oc}$  with application of an idealized "preference factor" obtained from free-energy relationships equal to 0.52, i.e.,

 $TBP = (C_s/f_{oc})/0.58$ 

ERDC/TN EEDP-01-47 May 2001

McFarland, V. A., Gibson, A. B., and Meade, L. E. (1984). "Application of physicochemical estimation methods to bioaccumulation from contaminated sediments. Steady-state from single-time-point observations," Willey, R. G., ed. Applications in Water Quality Control -- Proceedings. U.S. Army Corps of Engineers Committee on Water Quality, Hydrologic Engineering Center, Davis, CA, 150-167.

In this investigation Asiatic clams (*Corbicula fluminea*) and fathead minnows (*Pimephales promelas*) were simultaneously exposed to industrially contaminated river sediments. A simple kinetics model and physicochemical estimation methods were applied to bioaccumulation of PCB as total di- and total trichlorobiphenyls.

Results show that residues measured after a short exposure period, together with elimination rate constants ( $k_2$ ) estimated from octanol/water partition coefficients ( $K_{ow}$ ), can be used to approximate steady-state nonequilibrium tissue concentrations ( $C_{ss}$ ). The estimated  $C_{ss}$  values obtained using tissue residues ( $C_T$ ) measured after 7 days of exposure (t = 7), in the equation:

$$C_{ss} = C_T/(1 - e^{-k_2t})$$

agreed with  $C_{ss}$  values obtained using longer exposures and larger data sets at the  $\alpha \le 0.01$  level. Furthermore, normalization of residue data on tissue lipid content made comparisons of bioaccumulation between these dissimilar species possible.

McFarland, V. A., and Clarke, J. U. (1986). "Testing bioavailability of polychlorinated biphenyls from sediments using a two-level approach," Willey, R. G., ed. *Proceedings of 6<sup>th</sup> Seminar, Water Quality R & D: Successful Bridging Between Theory and Applications*. New Orleans, LA. U.S. Army Corps of Engineers Committee on Water Quality; Hydrologic Engineering Research Center, Davis, CA, 220-229.

Public laws (Section 404 of the Clean Water Act and 103 of the Ocean Dumping Act) regulating dredged material disposal require ecological evaluation prior to permitting of operations. Assessment of bioaccumulation potential of chemical contaminants in sediment may be required as a part of the evaluation process. Current methodology involves a 10-day exposure of aquatic organisms to contaminated sediment coupled with tissue analysis of the surviving organisms indicating detectable bioaccumulation. This procedure yields no information concerning chemical residues that could result in organisms exposed for prolonged periods to the sediments. There are no means of relating gross chemical contamination of sediments to concentrations that could result in exposed organisms, thus demonstrating a measure of the potential for bioaccumulation.

McFarland (1984) suggested a two-level approach for evaluating organic chemical contaminants in sediments. Level-I evaluation would be based on chemical phase distribution relationships and would use the results of sediment chemical analysis to estimate a theoretical maximum tissue residue resulting in an exposed organism if all the chemicals of interest in the sediment were bioavailable. Level II would follow if the maximum calculated in Level I were judged unacceptable, and this level could involve exposures of aquatic biota to the sediment as is done presently.

In this paper, the two-level approach is further described and results of an experiment involving exposures of freshwater fish and bivalve molluses to contaminated sediments are reported. The results illustrate the magnitude of the difference between Level I potential and Level II projected achievable contaminant bioaccumulation from sediments.

McFarland, V. A., and Clarke, J. U. (1987). "Simplified approach for evaluating bioavailability of neutral organic chemicals in sediment," *Environmental Effects of Dredging Technical Note EEDP-01-8*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 11 pp. http://www.wes.army.mil/el/dots/eedptn.html

This technical note outlines a tiered approach for evaluation of bioavailability of neutral organic contaminants in sediment and provides a method for the numerical expression of bioavailability. The first tier is a simple mathematical calculation, from sediment chemistry, of maximum potential bioaccumulation. If Tier I calculations indicate potential bioaccumulation of neutral organic contaminants to concentrations of concern, then Tier II laboratory tests could be conducted to determine the actual amount of bioaccumulation. In the second tier, bioaccumulation is assessed in laboratory exposures of organisms to the contaminated sediment. Comparison of the actual bioaccumulation at the projected steady state to the calculated maximum potential bioaccumulation results in a measure of bioavailability. An example is presented using laboratory exposures of an aquatic organism to harbor sediment contaminated with PCBs.

Clarke, J. U., McFarland, V. A., and Dorkin, J. (1988). "Evaluating bioavailability of neutral organic chemicals in sediments – a confined disposal facility case study," Willey, R. G., ed. *Proceedings of the Seminar: Water Quality* '88; February 23-25; Charleston, SC. U.S. Army Corps of Engineers Committee on Water Quality; Hydrologic Engineering Research Center, Davis, CA, 251-268.

A simple model for bioaccumulation potential and bioavailability of neutral chemicals from sediments was applied in a Chicago-area CDF case study. Analyses of fish and invertebrates taken from the CDF consistently reflected contamination of the sediments. Ratios of residues to sediment contamination were approximately constant regardless of species when concentration data were normalized on sediment organic carbon and on organism lipid. Steady-state conditions between sediment organic carbon and on organism contamination appear to exist within the CDF for all organisms analyzed, including those fish that normally are not thought to have direct contact with the sediments. Comparison of organism-residue: sediment-contamination relationships at sites outside the CDF indicated non-steady-state conditions where high sediment contamination existed. Higher tissue residues than those predicted by the model were found in biota taken from a site of low sediment contamination. This result is consistent with other recent laboratory and field results, but is not accounted for in the model.

McFarland, V. A., and Ferguson, P. W. (1994). "TBP revisited: A ten year perspective on a screening test for dredged sediment bioaccumulation potential," McNair, E. C., Jr., ed. DREDGING '94, Proceedings of the Second International Conference on Dredging and Dredged Material Placement, November 13-16, Lake Buena Vista, FL, Vol 1, 718-727.

A screening test for estimating bioaccumulation potential based on sediment chemistry and organism lipid content was proposed at "Dredging '84." The test, Theoretical Bioaccumulation Potential (TBP), has been included as a standard procedure in Tier II evaluations of dredged material in the Implementation Manuals for Section 103 of the Ocean Dumping Act (MPRSA of 1972) and the Clean Water Act (CWA of 1972) and is now widely used in regulatory evaluations to assess the suitability of dredged sediments for open-water disposal. Presently, the manuals recommend using a universal value, AF = 4, in the calculation. However, analysis of an extensive database of accumulation factors shows that value to be at the 94<sup>th</sup> percentile of the empirical values reported. Sources of variability in the AF are discussed and it is now apparent that far more realistic estimations of bioaccumulation potential can be made based on sediment chemistry by the use of empirical AFs in the calculation that are selected bearing in mind the nature of the chemical, the organism, and the exposure conditions.

McFarland, V. A. (1995). "Evaluation of field-generated accumulation factors for predicting the bioaccumulation potential of sediment-associated PAH compounds," *Technical Report D-95-2*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 158 pp.

Equilibrium partitioning of neutral organic chemicals between the organic carbon fraction of bedded sediments and the lipids of resident organisms provides the theoretical basis for one of the most popular approaches to the development of sediment quality criteria (SQC) by the U.S. Environmental Protection Agency (EPA). The proposed equilibrium partitioning-based SQC seek to relate estimated doses of sediment-associated chemicals to toxicity in exposed biota. Criteria documents for several polynuclear aromatic hydrocarbon (PAH) compounds, endrin, and dieldrin have been released by the EPA for public review, and may soon be promulgated. A procedure recommended in the Implementation Manual (the "Green Book") for public law regulating ocean disposal of dredged sediments (Section 103, Public Law 92-532, Marine Protection, Research, and Sanctuaries Act, the "Ocean Dumping Act") has used equilibrium partitioning-based estimations to screen sediments for bioaccumulation potential for several years. The screening test, termed "theoretical bioaccumulation potential," TBP, is also included in the draft manual for inland waters to implement dredged material testing requirements of the Clean Water Act. TBP employs an accumulation factor (AF), defined as the ratio at equilibrium of the organic carbon-normalized concentration of a neutral organic chemical in a sediment and the lipid-normalized concentration of the chemical in an exposed organism. The Green Book currently recommends using a universal AF = 4 for all neutral chemicals, the rationale being that this value is suitably protective of all neutral chemicals, provided certain caveats are recognized.

This study compared the predictive capability of PAH AFs derived from field data with that of the universal AF = 4 in making TBP estimations. Predicted bioaccumulations using the two methods were compared with PAH tissue concentrations measured in laboratory exposures of clams (*Macoma nasuta*) and mussels (*Mytilus edulis*). The empirical, field-generated AFs were highly predictive of actual bioaccumulation measured in the laboratory. Use of the universal AF = 4 substantially overestimated actual bioaccumulation.

McFarland, V.A. (1998). "Estimating bioaccumulation potential in dredged sediment regulation," *Proceedings of the USEPA National Bioaccumulation Conference, EPA 823-R-98-002*, U.S. Environmental Protection Agency, Bethesda, MD, 3.3-3.7.

The bioaccumulation of neutral organic chemicals in dredged sediments is estimated from sediment chemistry. A simple model is used in which concentration data are normalized on sediment organic carbon and organism lipid, and a biota/sediment accumulation factor (BSAF) is applied. This presentation describes research comparing predicted and actual measured tissue concentrations of polynuclear aromatic hydrocarbons (PAH) bioaccumulated from sediments by the clam *Macoma nasuta*.

Clarke, J. U., and McFarland, V. A. (2000). "Uncertainty analysis for an equilibrium partitioning-based estimator of PAH bioaccumulation potential in sediments," Environmental Toxicology and Chemistry 19(2), 360-367. Also published as: McFarland, V. A., and J. U. Clarke. (1999). "Analysis of uncertainty in TBP estimation of PAH bioaccumulation potential in sediments," Environmental Effects of Dredging Technical Note EEDP-04-32, U.S. Army Engineer Research and Development Center, Vicksburg, MS. 14 pp. http://www.wes.army.mil/el/dots/eedptn.html

In regulatory evaluations of contaminated sediments, an equilibrium partitioning-based screening test called theoretical bioaccumulation potential (TBP) is often performed to estimate the probable concentrations of neutral organic contaminants that would eventually accumulate in aquatic organisms from continuous exposure to a sediment. The TBP is calculated from contaminant concentration and organic carbon content of the sediment, lipid content of target organisms, and a partition coefficient, usually the biota-sediment accumulation factor (BSAF). However, routine applications of TBP have not included analysis of uncertainty. This paper demonstrates two methods for uncertainty analysis of TBP: a computational method that incorporates random and systematic error and a simulation method using bootstrap resampling of replicated model input parameters to calculate statistical uncertainty measures. For prediction of polynuclear aromatic hydrocarbon (PAH) bioaccumulation in bivalves exposed to contaminated sediments, uncertainty as a factor of TBP ranged from 1.2 to 4.8 using the computational method and 0.5 to 1.9 based on bootstrap 95 percent confidence intervals. Sensitivity analysis indicated that BSAF parameters, especially tissue contaminant concentration and lipid content, contributed In bootstrap tests of significance, TBP significantly over- or most to TBP uncertainty. underestimated actual PAH bioaccumulation in bivalves in 41 percent and 10 percent of comparisons, respectively.

## X. Trophic Transfer and Biomagnification

Suedel, B. C., Boraczek, J. A., Peddicord, R. K., Clifford, P. A., and Dillon, T. M. (1994). "Trophic transfer and biomagnification potential of contaminants in aquatic ecosystems," *Reviews of Environmental Contamination and Toxicology* 136, 21-89.

This review summarizes information obtained from published literature to determine to what degree biomagnification of organic compounds and metals occurs in freshwater and marine food webs. This review was conducted by: (1) examining data from studies conducted in laboratory

experiments to establish body burden ratios between trophic levels (trophic transfer coefficients; TTCs); (2) comparing laboratory-derived TTCs with data obtained from field studies; and (3) comparing biomagnification predictions described by published aquatic food-web models with data obtained in this review. It was determined that: (1) the majority of chemicals evaluated (both organic and metals) do not biomagnify in aquatic food webs; (2) for many of the compounds examined, considerable trophic transfer does occur in aquatic food webs; (3) DDT, DDE, PCBs, toxaphene, methyl mercury, total mercury, and arsenic have the potential to biomagnify in aquatic systems; (4) the lipid fraction of receptors directly influences biomagnification of lipophilic compounds; (5) the food web model reviewed provided similar estimates for most of the organic compounds examined (log K<sub>ow</sub> values between 5 and 7), with model predictions falling within the range of values of all compounds except dieldrin; (6) for many organic compounds, lack of information precludes assessing the relative importance of biomagnification for these contaminants; and (7) even those compounds for which evidence for biomagnification is strongest show considerable variability and uncertainty regarding the magnitude and existence of food-web biomagnification in aquatic systems.

Dillon, T. M., Suedel, B. C., Peddicord, R. K., Clifford, R. A., and Boraczek, J. A. (1995). "Trophic transfer and biomagnification potential of contaminants in aquatic ecosystems," Environmental Effects of Dredging Technical Note EEDP-01-33, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 12 pp. http://www.wes.army.mil/el/dots/eedptn.html

This technical note examines the potential of contaminants to biomagnify in aquatic ecosystems. This information will be useful in interpreting the environmental significance of regulatorymandated dredged material bioaccumulation test results. Several chemical classes were examined, with emphasis placed on contaminants that are of immediate concern for management of dredged material. The major classes of contaminants of concern for dredged material management include metals such as mercury and cadmium; polycyclic aromatic hydrocarbons (PAHs), especially petroleum-derived PAHs; known or potentially carcinogenic compounds such as dioxin; and organochlorine compounds such as polychlorinated biphenyls (PCBs). review was conducted in two phases. In Phase I, a literature review was conducted demonstrating contaminant trophic transfer or lack thereof in laboratory and field experiments. In Phase II, trophic transfer coefficients (TTCs) and estimates of overall potential for contaminant trophic transfer through aquatic food webs from Phase I were compared with appropriate data from published aquatic food web models. Phase II was designed to determine the applicability of laboratory and modeling results in predicting contaminant-specific trophic transfer potential.

**POINTS OF CONTACT:** For additional information contact one of the authors, Dr. Victor A. McFarland, (601) 634-3721, *mcfarlv@wes.army.mil*; or Ms. A. Susan Jarvis, (601) 634-2804, *jarviss@wes.army.mil*, or the manager of the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, (601) 634-3624, *englerr@wes.army.mil*.

**NOTE:** The contents of this technical note are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such products.

| AD NUMBER   | DATE               | DTIC   | ACCESSION |
|---|--------------------|--|-----------|
| 1. REPORT IDENT: FYING INFORMA  | TION               | REQUI  | 20        |
| A. ORIGINATING AGENCY US Army Engineer Res & D B. REPORT TITLE AND/OR NO ERDC/TN EEDP-01-47 | ev Center<br>JMBER | 1. Put yc<br>on rev<br>2. Compk<br>3. Attach | 0010      |
| C. MONITOR REPORT NUMBE   | R                  | maile<br>4. Use ui<br>inforr                 | )51       |
| D. PREPARED UNDER CONTR   | RACT NUMBER        | 5. Do not for 6                              | S         |
| 2. DISTRIBUTION STATEMENT   |                    | DTIC:  | 0         |
| Approved for public releadistribution is unlimite   | ase;<br>ed.        | 1. Assigi<br>2. Retur                        | 042       |
| OTIC Form 50  | PREVIOUS           | S EDITIONS ARE                               |           |

DTIC Form 50
JUL 96

PREVIOUS EDITIONS ARE OBSOLETE